Indian J. Phys. **51B**, 279-282 (1977)

Potential function of (X-H..X) hydrogen bonds

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The one dimensional potential model for hydrogen bonding has been used to calculate the different crystal structure and spectroscopic parameters associated with X-H . . X type H-Bonds in crystalline hydrogen halides and ice. It is found that the model potential cannot predict the intermolecular force and the hydrogen bond energy accurately. We suggest that the X-X electrostatic part of this potential should be modified to take account of the different higher order terms.

1. INTRODUCTION

The presently held view of the nature of hydrogen bonding is that it consists of four interactions. These are :

(1) electrostatic interactions, (2) nonbonded interactions including the attractive dispersion forces, (3) the short range repulsive forces and (4) the covalent charge transfer contributions. But there seems to be no unanimity in literature regarding the nature of hydrogen bonding. A faithful model potential function for hydrogen bonding X--H . . Y should reproduce the observed quantities like the X-H frequency shift, the intermolecular force for X—H . . Y—stretching, the hydrogen bond energy etc.

A model potential function given by Lippincott and Schroeder (1955) (hereafter refered to LS) for O—H—O bonding and later extended to N—H . . O, O—H . . N, N—H . . Cl, N—H . . N bonds is found to describe these observed features quite accurately (Schroeder and Lippincott 1957). This potential function has been very widely used for a number of hydrogen bonds (Reid 1959, King and Nixon 1968). Most of these calculations apply to organic systems, and very little attention has been paid to the intermolecular hydrogen bonding in hydrogen halide crystals. The Raman and infrared spectroscopy, X-ray and neutron diffraction experiment, dielectric constant measurements etc. provide enormous data for check of the applicability of a model potential to these X—H . . X (X=halogen) hydrogen bonds. In addition, it is to be noted that these small molecules HX possess large values of dipole and quadrupole moments, plarizabilities etc. In the present note,

we use the one dimensional model potential to see if it can satisfactorily reproduce the observed properties of X—H . . X bonds. In Section 2 we introduce the LS potential function, define the parameters and calculate the different quantities characterising the H bonds. In section 3 we discuss the failure of LS potential to reproduce all the features simultaneously and suggest some modifications which can improve the model potential for these strongly polar molecules.

2. The Lippincott—Schroeder Potential

The one dimensional potential defined by Lippincott and Schroeder for X—H . . X hydrogen bonds is

$$V(r,R) = V_1(r) + V_2(R,r) + V_3(R) + V_4(R) \qquad (1)$$

$$\text{where } V_1(r) = D_0^* \left[1 - \exp\left\{ - \frac{n(r - r_0)^2}{2r} \right\} \right]$$

$$V_2(R,r) = D_0^* \exp\left\{ \frac{-n^*(R - r - r_0)^2}{2(R-r)} \right\}$$

$$V_3(R) = Ae^{-bR} \text{ and } V_4(R) = B/R$$

r and R codrespond to the distances X—H and X .. X respectively, $n = K_0 r_0/D_0$ where K_0, r_0 and D_0 are respectively the force constant, internuclear distance and dissociation energy of the unperturbed X—H bond, D_0^* is the dissociation energy of the unperturbed $H—X^+$ bond, for which the force constant and internuclear distance are assumed to remain the same as in unperturbed X—H bond, hence $nD = n^*D_0^*$. Thus the first term represents a slightly stretched typical covalent bond X—H and the second term corresponds to the highly stretched bond $H—X^+$. The third term represents the Van der Waals repulsion between the halogen atoms and the last term is the electrostatic potential between the two halogen atoms.

We use the potential function defined by eq. (1) for the calculation of X-H distance, X—H frequency, X—H . . X stretching force constant and hydrogen bond energy for the intermolecular hydrogen in HF polymer, crystalline HF, HCl HBr and ice. The parameters K_0, r_0 and D_0 are obtained from standard works (Table—1), these parameters define the constant n. The constant n^* is chosen to give the best value of the X—H frequency shift, this constant in turn determines D_0^*; the constant A has been evaluated from the equilibrium condition $(dV/dR) = 0$. For the constant b we use the value 4.8 $Å^{-1}$ as suggested by LS. Thus the potential is completely defined. The calculated parameters are given in Table 2.

Table 1. Assumed parameters of LS potential

	F-H---F	Cl-H-----Cl	Br-H----Br	O-H----O
K_0 (mdyn/Å)	9.66(a)	4.81(b)	3.84(b)	7.76(c)
r_0 (Å)	0.917(b)	1.275(b)	1.413(b)	0.97(c)
D_0 (eV)	6.40(b)	4.43(b)	3.75(b)	5.12(c)
n^* (Å^{-1}) (d)	14.35	12.87	13.91	13.32
b (Å^{-1})	4.8(c)	4.8(c)	4.8(c)	4.8(c)
ω_0 (cm^{-1})	4140(a)	2889(b)	2559(b)	3700(c)

(a) Coulson 1953.
(b) Herzberg 1935.
(c) Lippincott and Schroeder (1955)
(d) Adjusted values.

3. Discussion and Proposed Modification of LS Potential

The good agreement with the observed values for both X—H frequency and X—H distance shows that the properties of internal X—H bond are described well by the LS function. But in case of intermolecular X . . X bonds the agreement is good only for the X . . X stretching force constant K_x. Although the experimental values of hydrogen bond energies are not available for all the cases considered, yet it is found that in the two cases of HF polymer and ice, for which these values are available, the agreement is not at all good. A readjustment of the value of the constant b can be done to improve the agreement of hydrogen bond energy, but this will be associated with a decrease in the agreement of the force constant K_x.

This failure of the LS function to reproduce both the energy and the force constant of the hydrogen bond may be inherent in the choice of X—X electrostatic term in the LS function. The choice of R^{-1} type term is explained by LS as arising due to fractional charges on the two X atoms. This may be true, but, as has been argued by Reid (1959), R^{-6} type dispersion term should also be important.

Table 2. Parameters calculated with LS potential

Molecular System	R (Å)	X-H frequency (cm^{-1})		X-H distance (Å)		X-H Stretching force constant (mdyn Å)		H-bond energy Kcal	
		Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs
HE polymer	2.55[a]	3427	3440[b]	0.96	1.00 ± 0.06[a]	0.31	—	4.32	6.7[a]
HF Solid	2.51[c]	3258	3065[d] 3404	0.97	0.97 ± 0.01[c]	0.50	0.54[d]	5.34	—
HCl Solid	3.688[e]	2730	2708[f] 2748	1.29	1.25 ± 0.02[e]	0.047	0.06[g]	1.09	—
HBr Solid	3.961[h]	2422	2466[f] 2440	1.43	1.38 ± 0.03[h]	0.029	0.05[g]	0.81	—
Ice	2.76[i]	3209	3200[i]	1.0	1.0[i]	0.21	0.22[i]	3.27	5.8[i]

(a) Pauling 1966, (b) Coulson 1953, (c) Johnson, Sandor and Arzi 1975, (d) Kittelberger and Hornig 1967, (e) Sandor and Farrow 1967, (f) Savoie and Anderson 2966, (g) Ito *et al.* 1969, (h) Sandor and Johnson 1968, (i) Lippincott and Schroeder 1955, (j) Grahn 1953.

We feel that since the X-H donor group in a hydrogen bond X-H . . X is very strongly polar (i.e. have permanent molecular moments), their moments will interact with the charge of the acceptor atom X. This would mean that one should consider the higher order terms in an expansion of the Coulombic interaction. Thus the electrostatic part of the potential, V_4, should be modified to incorporate the terms depending on higher inverse powers of R. This may be taken as

$$V_1(R) \quad -\sum_{m=1}^{\mu} B_m/R^m$$

Where μ is the maximum value of m i.e. the maximum number of terms one can retain in the series. Calculations with this and other modified forms of LS function are being done by us and will be reported elsewhere.

The author thanks the Computer Centre, Calcutta University for providing computation facilities. The author thanks Professor P. C. Bhattacharya for his encouragement and Professor D. L. Bhattacherya for helpful comments.

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